"Faster G0W0 implementation for more accurate photovoltaic material design"

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Density-functional theory (DFT) is currently the ab initio method most widely used to predict electronic energy levels of new molecules. However, approximations intrinsic to the theory limit the accuracy of calculated energy levels to about ±0.5 eV. More efficient theoretical design of molecules and polymers of interest to photovoltaic applications could be achieved if more precise ab initio methods were available. The G0W0 approach is an ab initio method that provides such an enhanced precision, with predicted energy levels precise to about ±0.05 eV. However, such calculations are currently prohibitive for systems with more than a few hundreds of electrons, thus limiting their use in the photovoltaic community. What limits calculations to this system size is the need in current implementations to invert the dielectric matrix and the need to carry out summations over conduction bands. This poster presents a strategy to avoid both of these bottlenecks. Preliminary results will be pr...

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Faster G_0W_0 implementation
for more accurate photovoltaic material design

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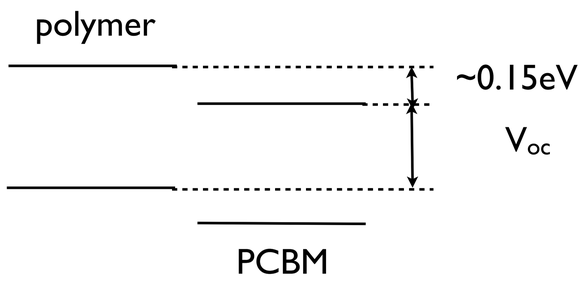
Abstract

Density-functional theory (DFT) is currently the *ab initio* method most widely used to predict electronic energy levels of new molecules. However, approximations intrinsic to the theory limit the accuracy of calculated energy levels to about ±0.5 eV. More efficient theoretical design of molecules and polymers of interest to photovoltaic applications could be achieved if more precise methods were available. The G_0W_0 approach is an *ab initio* method that provides such an enhanced precision, with predicted energy levels accurate to about ±0.05 eV. However, such calculations are currently prohibitive for systems with more than a few tens of electrons, thus limiting their use in the photovoltaic community. What limits calculations to this system size is the need in current implementations to invert the dielectric matrix and the need to carry out summations over conduction bands. This poster presents a strategy to avoid both of these bottlenecks.

Introduction

Using *ab initio* calculations to guide synthesis:

$$PCE = \frac{V_{oc} J_{sc} FF}{1000 W / m^2}$$



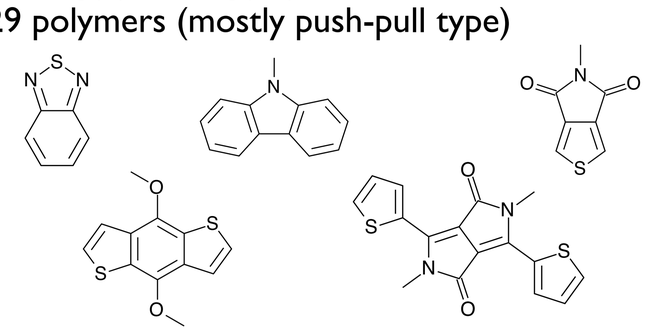
Assessing the efficiency of a polymer before synthesis requires precise calculations of the V_{oc}, which requires precise calculation of the HOMO and LUMO energies of the polymer.

Ab initio methods can do this:
- DFT : fastest, but accurate enough?
- G_0W_0 : more accurate, but unwieldy.

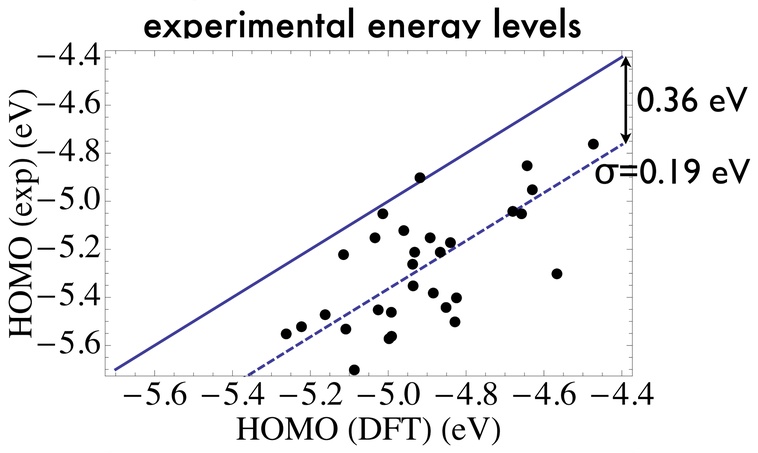
DFT accuracy

Is it accurate enough for polymer design?

Methodology :
- B3LYP functional
- Gaussian 03/09 code
  6-311g(d)/6-311g(2d) basis set
- 29 polymers (mostly push-pull type)



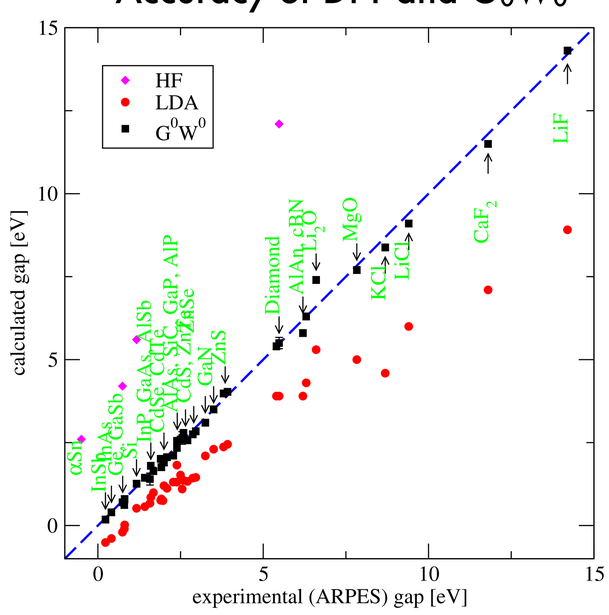
Comparison between DFT and experimental energy levels



The G_0W_0 method

DFT levels offer quick sorting of candidate polymers.
Further refinement is still desirable given the ressources and time required to synthetise a new polymer.
G_0W_0 can provide such results

Accuracy of DFT and G_0W_0



In G_0W_0, DFT eigenstates and eigenvalues are used as a starting point :

$$\left(\hat{T} + \hat{V}_{ext} + \hat{V}_{xc}\right)\left|\phi_i\right\rangle = \varepsilon_i^{DFT}\left|\phi_i\right\rangle$$

They are then corrected to first order in perturbation theory using the GW exchange-correlation operator Σ(ω) :

$$\varepsilon_i^{G_0W_0} \approx \varepsilon_i^{DFT} + \left\langle\phi_i\right|\hat{\Sigma}(\varepsilon_i^{G_0W_0}) - \hat{V}_{xc}\left|\phi_i\right\rangle$$

The expectation value of Σ(ω) being :

$$\left\langle\phi_i\right|\hat{\Sigma}(\varepsilon_i)\left|\phi_i\right\rangle = \frac{i}{2\pi}\sum_{n}\int_{-\infty}^{+\infty} d\omega \frac{\left\langle\phi_i\right|\left\langle\phi_n^*\right|\hat{\epsilon}^{-1}(\omega)\hat{v}\left|\phi_n^*\right\rangle\left|\phi_i\right\rangle}{\omega - (\varepsilon_n - \varepsilon_i)}$$

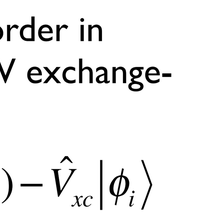
where $\hat{v}$ is the coulomb operator and where :

$$\hat{\epsilon}(\omega) = \hat{1} - \hat{v}\hat{P}(\omega)$$

$$\hat{P}(\omega) = \sum_{cv}\left|\phi_c^*\right\rangle\left|\phi_v\right\rangle\left[\frac{1}{\omega - (\varepsilon_c - \varepsilon_v)} - \frac{1}{\omega + (\varepsilon_c - \varepsilon_v)}\right]\left\langle\phi_v\right|\left\langle\phi_c^*\right|$$

○ : bottleneck #1 : sum over conduction states
○ : bottleneck #2 : inversion of the dielectric matrix

Problematic example : C_{60}



$N_c \approx 10N_v$ = 1200 & 300 000 planes waves

⇓

$\{\varphi_c, \varepsilon_c\}$ ⇒ 9 Gb RAM & days of CPU time

$\hat{\epsilon}(\omega)$ is 10 000 x 10 000 in planewave basis

⇓

$\hat{\epsilon}^{-1}(\omega)$ ⇒ 1,5 Gb RAM & days CPU time

Solution to bottleneck 1

Sternheimer equation

Idea : transform $\sum_c$ into a linear equation problem...

$$\hat{P}(\omega)\left|\psi\right\rangle = \sum_{c,v}\left|\phi_c^*\right\rangle\left|\phi_v\right\rangle\left[\frac{1}{\omega - (\varepsilon_c - \varepsilon_v)} - \frac{1}{\omega + (\varepsilon_c - \varepsilon_v)}\right]\left\langle\phi_v\right|\left\langle\phi_c^*\right|\left.\psi\right\rangle$$
$$\equiv \sum_v \left|f_v^{+*}v\right\rangle + \left|f_v^{-*}v\right\rangle$$

$$\Rightarrow \left|f_v^{\pm}\right\rangle = -\sum_c \frac{\left|\phi_c\right\rangle\left\langle\phi_c\right|}{\varepsilon_c - \varepsilon_v \pm \omega}\left|\psi^*\right\rangle\left|\phi_v\right\rangle$$
$$= -\sum_c \frac{\left|\phi_c\right\rangle\left\langle\phi_c\right|}{\hat{H} - \varepsilon_v \pm \omega}\left|\psi^*\right\rangle\left|\phi_v\right\rangle$$
$$= -\frac{\hat{P}_c}{\hat{H} - \varepsilon_v \pm \omega}\left|\psi^*\right\rangle\left|\phi_v\right\rangle$$

⇒ Eliminating $\sum_c$

$$\Rightarrow \left(\hat{H} - \varepsilon_v \pm \omega\right)\left|f_v^{\pm}\right\rangle = -\hat{P}_c\left|\psi^*\right\rangle\left|\phi_v\right\rangle$$ (Sternheimer's equation)

Implementation of solution

1) H is sparse ⇒ iterative method

2) H - $\varepsilon_v \pm \omega$ can be singular ⇒ SQMR instead of CG

Solution to bottleneck 2

Lanczos algorithm

Usually, $\hat{\epsilon}(\omega)$ is expressed in a planewave basis.
Here, we decrease the size of the matrix by constructing a basis that automatically focuses on the relevant subspace :

$$\left\{\left|\phi_0\right\rangle, \hat{\epsilon}(\omega)\left|\phi_0\right\rangle, \hat{\epsilon}^2(\omega)\left|\phi_0\right\rangle, ..., \hat{\epsilon}^N(\omega)\left|\phi_0\right\rangle\right\}$$

and then orthonormalize it to obtain the Lanczos basis :

$$\left\{\left|l_0(\omega)\right\rangle, \left|l_1(\omega)\right\rangle, \left|l_2(\omega)\right\rangle, ..., \left|l_N(\omega)\right\rangle\right\}$$

which is substantially smaller than a planewave basis of equivalent accuracy.

Example : silane		
	Conventional implementation	Present implementation
$\hat{\epsilon}(\omega)$	6000 x 6000	200 x 200
N	3000	-
CPU time	~48h	~8h

Conclusion

- DFT calculations are useful for sorting a large group of candidate polymers.
- Further refinement of calculations using G_0W_0 would be desirable, but unwieldy with current implementations due to 2 bottlenecks :
  1. The sum over conduction states
  2. The inversion of the dielectric matrix
- We assess these bottlenecks using :
  3. Sternheimer's equation
  4. Lanczos algorithm
- and obtain a 6-fold increase in speed

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